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## OCCURRENCE OF MANGANESE IN WATER.

By C. C. YOUNG, University of Kansas, Lawrence.

IN THE work of the Kansas Water Survey the presence of manganese was indicated in several waters that had been submitted for examination. Owing to the small amount of data relating to manganese-containing waters in this country it is thought well worth while to follow up the hint thus given. This article is in the main a statement of results obtained before making a complete survey of the ground-water supplies of the state in regard to manganese.

The presence of manganese in ground waters is due to the same causes that effect the solution of iron so commonly found in waters from river valleys. Manganese usually exists in these valley soils in the form of oxides or basic carbonate, and as surface water percolates through the soil containing unoxidized organic matter it is deprived of its free oxygen. When the free oxygen is used up from the water, the soluble organic matter attacks the oxides of iron and manganese and reduces them to a ferrous and manganous condition, when solution is then effected by the carbonic acid naturally present in the water.

Whenever the amount of iron and manganese so dissolved exceeds 0.5 to one part per million, the taste and value of the water for domestic purposes is impaired. At Hutchinson, Kan., in 1904, the service pipes of the water company were completely stopped up by an earthy brown deposit which, according to Dr. E. H. S. Bailey,<sup>1</sup> contained 45.2 per cent  $Mn_3O_4$ . The water causing this deposit contained only one part per million of manganese. Often deposits are caused by the presence of *Crenothrix*.

Waters containing these soluble salts are clear when drawn, but become very turbid on standing, due to the absorption of oxygen from the air and conversion of manganese into the hydroxides, which, on standing, will settle out as rusty precipitate. It has been shown<sup>2</sup> at Berlin, Brunswick, Hanover and several other places that the ferric hydroxide precipitates out faster than the manganic

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1. *Jr. Amer. Chem. Soc.*, vol. XXVI, No. 6.

2. *Trans. Amer. Soc. Civil Eng.*, vol. LXIV, p. 173.

hydroxide. This is illustrated by some laboratory experiments made on the Lawrence (Kan.) waters:

TABLE I.

	Parts per million.	
	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	Manganese.
No. 25 (a) Taken from well.....	14.8	2.62
(b) After standing 48 hours.....	5.2	1.04
No. 26 (a) City water, after treatment before settling .....	14.4	2.51
(b) After standing 48 hours .....	3.2	.93

Sample No. 25 was taken directly from the large well from which a great portion of the city supply is drawn.

Sample No. 26 was taken from the outlet to the settling basin after the water had been treated with a small amount of lime and aerated. In both cases the waters were allowed to stand forty-eight hours and the clear solution above the precipitate pipetted off. The results above are the average of several analyses.

However, the ratio of the iron to the manganese removed from the water as delivered to the consumer is different, there being a larger per cent of manganese removed than iron. Results of analyses made on seven different days on the tap water showed an average of 1.16 parts per million of manganese and 10 parts per million of iron and aluminum oxides. The tap water thus contained about three times as much iron and aluminum oxides as the water which had settled in the laboratory. This discrepancy was due, no doubt, to a larger amount of the ferric hydroxide remaining in suspension, the first deposit carrying down the precipitated manganese, or the unoxidized organic matter still in the water has a tendency to keep the iron in solution while in contact with the iron pipes of the system, there being no solution of manganese going on while in the pipes.

The difficulty of determining manganese by long gravimetric methods, or by volumetric methods of doubtful accuracy in cases of small amounts of manganese, was obviated by making use of the bismuthate methods as adapted to waters by Mr. Robert Spurr Weston,<sup>3</sup> with a slight modification on account of the high chlorine in the Kansas waters. The method used in this work is as follows:

Evaporate with 5 cc. of concentrated sulphuric acid to strong fumes, 250 cc. of the water of unknown manganese content. Take up with 50 cc. of nitric acid (sp. gr. 1.135), and when the solution is cold add about 0.5 gram of sodium bismuthate. Heat until the pink color disappears, with or without the precipitation of manga-

3. *Jr. Amer. Chem. Soc.*, vol. XXIX, p. 1073; *Blair, Chem. Anal. Iron and Steel*, p. 135; *Chem. News*, vol. LXXIV, pp. 247-302, vol. LXXXV, p. 59; *Trans. Chem. Soc.* 1895, p. 268; *Ding. Poly. Jr.*, pp. 224-269; *Brearley & Ibbotson, That Anal. of Street Wks. Materials*.

nese dioxide. If the solution is colored brown, add enough ammonium ferrous sulphate to clear the solution, and boil off any oxides of nitrogen. Add a drop of silver nitrate to remove from the solution the last trace of chlorides. Cool to about 16° and add an excess of sodium bismuthate, shake for a few minutes, and filter through a washed asbestos mat free from organic matter. Wash the filter with three-per-cent nitric acid solution, then transfer to a large Nessler tube and make up to 100 cc. Run into another 100-cc. tube, containing sulphuric acid solution made very slightly pink with permanganate, enough standard potassium permanganate solution to match the color of the sample.

TABLE II.

SOURCE OF SUPPLY.			Manganese, parts per million.	
			1.	2.
1.	Chanute	Well No. 7	0	0
2.	Chanute	Well No. 8	0.074	0.074
3.	Chanute	Well No. 9	0.186	0.140
4.	Barnes	Well	0	0
5.	Barnes	City well	0	0
6.	Lucas	Well	0	0
7.	Lucas	Well	0	0
8.	Lucas	Well	0	0
9.	Lucas	Well	0	0
10.	Lucas	Well	0	0
11.	Excelsior Springs, Mo.	Ferro-Mn. water	3.86	4.00
12.	Excelsior Springs, Mo.	Ferro-Mn. water	Trace.	Trace.
13.	Excelsior Springs, Mo.	Ferro-Mn. water	0	0
14.	Garden City	Well	0	0
15.	Garden City	Well	0	0
16.	Garden City	Well	0	0
17.	Burlington	Well	0	0
18.	Burlington	Well	0	0
19.	Burlington	Well	0	0
20.	Burlington	Well	0	0
21.	Wakefield	Well	0.26	0.26
22.	Wakefield	Well	0	0
23.	Horton	Well	0.036	0.036
24.	Lawrence:			
	(a) Dec. 11, 1909	Tap water	1.34	
	(b) Dec. 13, 1909	Tap water	1.12	
	(c) Dec. 14, 1909	Tap water	1.30	
	(d) Dec. 16, 1909	Tap water	1.19	
	(e) Dec. 17, 1909	Tap water	0.74	
	(f) Dec. 20, 1909	Tap water	1.15	
	(g) Dec. 21, 1909	Tap water	1.30	
25.	Lawrence	Main well	2.60	2.64
26.	Lawrence	City water after treatment before settling	2.51	2.51
27.	Topeka	Tap water	0.74	0.74
28.	Bonner Springs	Tap water	0.52	0.59
29.	St. Marys	Tap water	Trace.	Trace.
30.	Wamego	Tap water	Trace.	Trace.
31.	Hays	Well	0.55	0.56

The results of the examination of twenty-nine different ground waters from Kansas and western Missouri show the presence of manganese in twelve cases, and a sufficient amount in a few cases to make the water undesirable for a city supply on account of the tendency for "*Crenothrix<sup>4</sup> ananganfera*" to grow, if for no other

4. Jr. Soc. Chem. Ind., 21-681; Trans. Amer. Micro. Soc., 23-32; Bot. Zeit. 1888, bd. 46.

reason. However, at the time these analyses were made no *Crenothrix* could be found in the Lawrence supply, but at certain times of the year this supply is usually troubled with the growth.

From what has been said one might be led to think that all waters containing iron in considerable quantities contain manganese also, but the waters having no manganese in the table above were introduced to illustrate this point.

All of the twenty-nine supplies examined contained more than two parts per million of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . The best illustration of waters with iron and no manganese are the Lucas waters.

TABLE III.

	Parts per million $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$
No. 6.....	14.4
No. 7.....	4 4
No. 8.....	5.2
No. 9.....	5.8
No. 10.....	Not determined.

The waters showing the greatest amount of manganese are the ones whose sources are the water-bearing sands and gravel of the Kaw river valley.

It has been observed in the city water supplies along the Kaw river that the rusty iron precipitate does not show up until the supply has been in use for some time.

At the present time the village of Bonner Springs is considering the abandonment of the present source on account of the large amount of iron and manganese present, as the cost of maintaining a filter plant or any other method of purification would be too great.

The plants longest in operation along the Kaw show the most manganese. The Lawrence and Topeka works were put in operation about the same time. Wamego was next, with Bonner Springs and St. Marys last, in the order given. The time is not far distant when the larger towns will be compelled to put in operation some form of purification other than settling the water, for at times when the organic matter is high in the water scarcely any of the iron is removed by the slight aeration and settling now given it. The private wells in Topeka and Lawrence are so badly polluted that a good supply will be demanded for domestic uses before many years.

N. B.—In the last volume of the Transactions of the American Society of Civil Engineers (September 19, 1909), there is a complete discussion of iron and manganese removal, as practiced in this country and abroad, by Mr. Robert Spurr Weston.

December 21, 1909. Water Survey Laboratory, University of Kansas.